

Small metal particles of nanometer size are of great scientific interest regarding their solid state properties as well as for the application as catalysts. They offer a promising approach to study structural effects with relevance for a variety of applications in chemistry as well as in physics.

The properties of *individual* particles which typically have dimensions in the nanometer range can be investigated by using scanning probe microscopic techniques. Typically, a large number of particles with uniform size and structure are needed for electrochemical investigations.

When the catalytic properties of supported clusters are measured by standard electrochemical methods as cyclic voltammetry or oxidation transient measurements only the average properties of the entire distribution of particles on the electrode surface are measured. In order to investigate the local reactivity of platinum clusters and to obtain a correlation with its structure, the STM tip electrode can be used as a local sensor using hydrogen evolution and oxidation as model reaction. To avoid interference from different particles and to be sure to characterize only the hydrogen produced by a single particle it is essential to use electrodes with a very low particle density on an inert surface.

Palladium is deposited in-situ using the STM tip following the method of Kolb et al. [1] on a gold surface which is mainly (111)-oriented. First, palladium is deposited in an external electrochemical cell onto the tip from a PdSO_4 solution. Then the tip is mounted on the STM and introduced into the electrochemical cell. A nanoparticle is produced by a tip approach and a typical image of a tip-generated particle is seen in Figure 1. The particle structure and size depends on numerous parameters and the tip structure is probably the most important. At present, the tip structure cannot be controlled sufficiently to ensure a reproducible particle generation. Therefore the procedure yields particles of different structure and sizes. However, this variation in size and structure enables us to investigate the influence of the structure on the reactivity of particles. For example, also structural changes - like a broadening of the particles during the measurement - can be correlated with reactivity changes. The result of several measurements concerning the reactivity of hydrogen evolution on different palladium particles with different structures is shown in figure 2.

A constant distance from the particle surface can be adjusted by using the STM in constant current mode. The potentials of the substrate and the STM tip are kept at a value where no reactions take place. After switching off the feedback regulation and retracting the tip out of the tunneling distance the potential of the platinum particle is set to a value where hydrogen is produced while the potential of the tip is held at a value where hydrogen can be oxidized. The feasibility of this approach was demonstrated when comparing the currents detected over a particle and over the bare gold surface. Whereas in the first case currents in the range of 0.1 - 1 nA can be detected over the bare surface only currents in the order of

10 - 100 pA are measured. The high observed current over the particles can be explained by three-dimensional diffusion at the particle and the tip. A strong dependence of the detected current on substrate potential is observed and also displayed in Figure 2. Due to the nanometer dimensions of the system and the very effective three-dimensional diffusion, mass-transfer limitation do not exhibit an influence over a large potential region. The kinetic domain of the reaction can be investigated straightforwardly with this method. Most interesting is that the structure and size of the palladium particles has a pronounced influence on the hydrogen evolution reaction. Small structures shown a pronounced enhancement in the current densities as well as in the exchange current density compared to large palladium particles which are assumed to exhibit the bulk properties. Also, structural changes which can occasionally be observed during the measurement, e.g. a broadening of the nanoparticle into a two-dimensional island - are accompanied by pronounced changes in the current density.

This indicates that it is indeed possible to measure the reactivity of single particles and deduce kinetic information regarding the reactions and determining the influence of the surface and particle structure.

The possibilities and limitations of the approach will be discussed and several models to explain the observed effects will be presented.

References

- [1] G. E. Engelmann, J.C. Ziegler, D. M. Kolb, J. Electrochem. Soc. **145** (1998) L33

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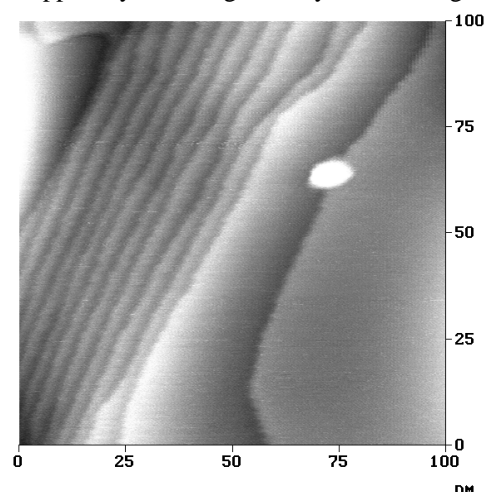


Figure 1: Typical image of a particle generated by a tip approach.

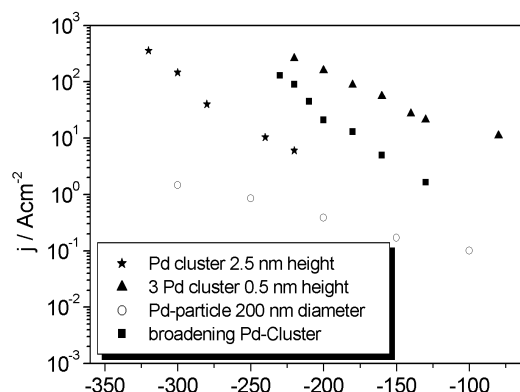


Figure 2: Tafel plot for the hydrogen evolution reaction of different palladium particles generated by tip approach. Influence of their structure and size.